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RESEARCH ARTICLE **(Open Access)**

Development of a sequential extraction method for different forms of phosphorus in Bovilla lake sediments

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1. Abstract

Extractable forms of phosphorus are studied more widely than the extractable forms of most other elements. The main reason for this is because P is the key element in aquatic chemistry of lakes being a limiting nutrient in the growth of algae under many conditions. Exchange with bottom sediments place an important role in making P available for algae and contributes, therefore to eutrophication. Many extraction schemes have been developed to determine different forms of P in sediments. The objective of the present study was to estimate the bioavailability/mobility of phosphate from Bovilla lake sediments using a sequential extraction procedure and to evaluate their possible contributions to the P-loadings the lake. Results for three stations of Bovilla Lake are presented. A relatively high total phosphorus content of 452 mg/kg DW have been found in sediment samples taken from three sites of Bovilla Lake. This shows an important potential of sediments to release the P compounds, especially under anoxic conditions.

Keywords: lake sediment, phosphorus, sequential fractionation

1. Introduction

Sediments play a fundamental role in determining concentration, distribution and the final fate of several pollutants acting as a principal transport vehicle and the site of accumulation or release [21]. Phosphorus is often the limiting nutrient for algal growth in lakes and may limit marine productivity [1]. Phosphorus may enter an aquatic system in the particulate form or dissolved-P may become associated with particles as they settle out of the water column [18]. Sedimentation is a major P sink for the epilimnia of lakes, transporting P to the hypolimnion and ultimately the sediments [13]. The long-term contribution of sediment bound P in promoting eutrophication of freshwater can be more efficiency evaluated on the basis of different P-fractions instead of total phosphorus content, since the total concentrations of phosphorus in sediments cannot predict the potential ecological danger [17]. Physical and chemical characterization of sediments is important for evaluating the phosphate exchange processes between bottom sediments and overlying [10]. In many lakes a significant fraction of the annual phosphate loading accumulates in the sediments. Depending upon environmental conditions, partial release of these phosphates may occur [20]. Solubility of phosphate in the interstitial water of sediment under prevailing conditions of pH, redox potential and ionic strength is controlled by the chemical composition of the phosphates present and their interactions with other minerals or amorphous materials [14]. The association of phosphate with iron, aluminum and calcium, and the adsorptive properties of carbonates and clays are of special interest [12]. Since the amount of phosphorus release from sediment is called internal phosphorus loading, which can enhance lake eutrophication, the fractionation of sediment P can be conducive to understanding P cycling in the aquatic ecosystem [8]. Phosphorus release is a function of the quantity and distribution of phosphorus fractions within the sediments, the degree of saturation of exchangeable phosphorus and of hydrological conditions [9, 19, 3].

Several extraction schemes have been developed to elucidate the chemical nature of sediment phosphates [10, 23, 16]. Sequential extraction of P as suggested by several authors is a useful tool for characterisation of various P compounds [5, 6, 17, 23]. Chemical fractionation, involving sequential extraction procedures, is based on differences in reactivity of solid phases to different extractant solutions.

2. Materials and methods

2.1 Site description

Bovilla reservoir is the main source of drinking water for the city of Tirana. The reservoir was constructed in 1998, located about 15 km North-East of Tirana city. It has a surface of 4575 km^2, maximum volume of 80.6 km^3, and average depth of 18 m. The Bovilla Lake profiles, from the limnological point of view, were characteristic for a deep reservoir similar

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to a classical lake. Vertical thermal stratification was observed from late spring up to early fall, and only one mixing developed beginning in late fall and remaining up to early spring. The predominant trophic state of Bovilla Lake was oligotrophy, with relatively high levels of dissolved oxygen in the hypolimnion layers, low nutrient levels and from applications of various evaluation models.

2.2 Sediment samples and procedure

Sediment samples were collected using a grab sampling device. The samples were air dried, homogenized by grinding and finally passed through a 75 *µ*m sieve and stored in glass bottles. Analysis of the fraction <75 *µ*m is recommended in sediment studies because clay and silt particles generally contain the highest concentrations of pollutants, and are most readily transported in suspension in natural waters.

In order to characterize various P-species in lake sediments, a sequential extraction scheme according to Harmonized protocol BCR (STM 1998) developed by the European Commission for determination of total P, Inorganic and Organic P, and NaOH extractable and acid (HCl) extractable P, was used (presented in Table 1). In each fraction, soluble reactive P (SRP) was determined after filtration through a pre-rinsed 0.45 *µ*m membrane filter according to the molybdenum blue/ascorbic acid method [2]. Sediment was also analyzed for dry weight (DW) by drying at 105 ˚C for 2-4 hr.

Table 1: The phosphorus sequential extraction procedure used in this study.

Fraction	*Procedure*
Total	Ignited at 450˚C, 3 h; +HCl 3.5 M; shake for 16 h; centrifuge at 2000 rpm for15 min
Inorganic	+ HCl 1M; shake for 16 h, centrifuge at 2000 rpm for 15 min
Organic	Residue from step 2: wash by water (twice) centrifuge for 15 min; Dry the precipitate at 80 ^{0}C, calcinate at 450˚C for 3h; + HCl 1M; stir for16 h; centrifuge at 2000 rpm for 15 min
Iron-Bonded P (NAIP)	+ NaOH 1M,stir for16 h, centrifuge at 2000 rpm for 15 min; extract + HCl 3.5 M, after 18 h at rest, centrifuge at 2000 rpm for 15 min
Ca- Bonded P (AP)	Residue from step 4: wash by NaCl 1M (twice), stir for 5 min, centrifuge; residue +HCl 1M , stir for 16 h, centrifuge at 2000 rpm for 15 min

When considering P-franctions and their mobilization, there is a need to know how much (or what fraction) of the sediment can be available to algae and/or bacteria. According to Bostrom *et al.* (1982), a good approach would be to consider all P that can be released within the occurring ranges of temperature, pH and redox as bioavailable.

3. Results and Discussion

Results of different forms of phosphorus in Bovilla lake sediments samples studied are demonstrated in the graph below (Figure 1).

This is an unexpected result, because phosphorus concentrations in water of Bovilla lake ranged from less than 2 µg/l to 14.7 µg/l; arithmetic mean concentration is 4.85 µg/l. Mean values were a little higher at site 2 and 3 (Figure 2), which are in littoral zone.

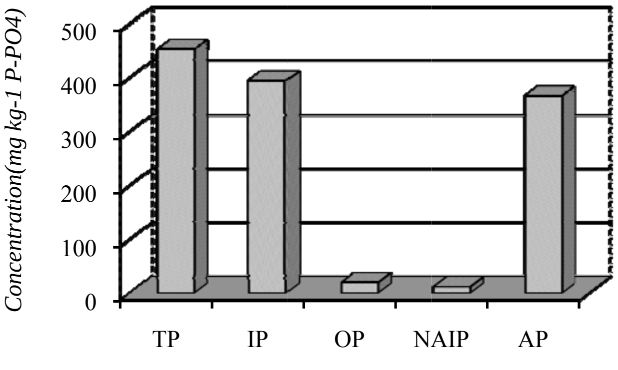

Figure1. Mean concentration of P forms in Bovilla lake sediments

As we can see a relatively high total phosphorus content (452 mg/kg DW) have been found in sediment samples taken from three sites of Bovilla Lake, the same level as mesotrophic to eutrophic lakes.

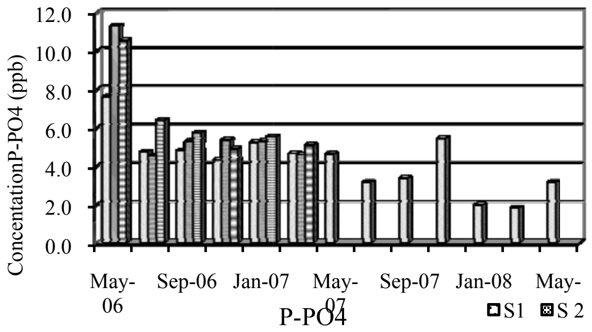

Figure 2. Mean phosphorus concentration in water of Bovilla lake

Results of nearly all water samples were less than 10 μg/l proving a visible oligotrophic situation according OECD– 1982 limit values and UNECE Guidelines but also according EEA 1982 limits of 3 to 25 mg/m^3. There are not big differences between levels during overturn and stratification periods, even some higher levels are observed during overturns. This means that the contribution from internal loading is constant and relatively low during all periods because anoxic conditions were not observed in water layers near sediment.

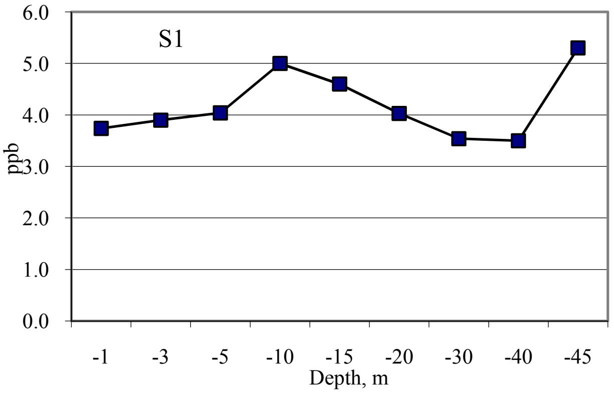

Figure 3. Variation of overall mean concentration of phosphorus with depth

As can be seen from Figure 3, phosphorus concentration fluctuated with depth presented a maximum at about 10 meters. Mean concentration in epilimnetic layer (1-15 m) is 4.3 ppb whereas in lower layers (20-40 m) is 3.7 ppb. The higher concentration near the top of the lake reflects the increased content of organic matter – algae but also particulate solids. Since decomposition of organic matter occurs to a larger extent on the bottom of the lake, available P concentration is higher in the water layer in contact with sediment bottom (mean concentration 5.3 ppb in depth 45 meters).

4. Conclusions

A sequential phosphorus fractionation procedure was used to examine the forms of P in Bovilla lake sediments to determine the potential bioavailability. The main part of the P in sediments is present in inorganic form (soluble in HCl 1M), which constitutes about 87% of the amount. Around 93% of it is associated with calcium (AP) and is considered nonavailable. Only a small part, about 3% of it is associated with iron (NAIP) and is considered as bioavailable. A small part of P in sediments is present as organic matter (around 4.3 % of total content); this is explained not only with a small quantity of the content of algae in the lake but also the removal of phosphorus with water that obtained from the treatment plant.

Phosphorus concentration in sediments is relatively high (452 mg/kg DW). This can be considered very dangerous, because insoluble phosphorus forms undergo bacterial decomposition (mineralization) and the phosphorus could be transformed into the soluble orthophosphate to the water deteriorationing the trophic state and the quality of the water.

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